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**EPO FORM 10079**

## INTERNATIONAL SEARCH REPORT

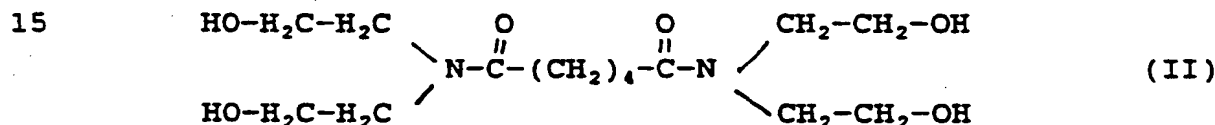
International Application No

PCT/NL 93/00155

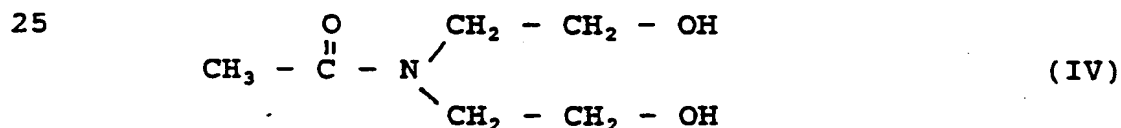
<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09D5/03; C09D133/06; C09D167/02		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification Systems	Classification Symbols	
Int.Cl. 5	C08K ; C09D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	EP,A,0 473 380 (ROHM AND HAAS COMP) 4 March 1992 scheme 2  -----	1
<p><sup>10</sup> Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
20 OCTOBER 1993	- 9. 11. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	Dieter Schöler	

functionalities, the first compound having a  $\beta$ -hydroxyalkylamide functionality of  $\geq 3$  and the second compound having a  $\beta$ -hydroxy-alkylamide functionality of  $\leq 3$ , as a crosslinker in the preparation of powder coatings.

8. Use according to claim 7, characterized in that the first compound has a functionality of 4 and the second compound has a functionality of 2.
9. Powder coating composition, crosslinker and use according to any one of claims 1-8, characterized in that the first compound having a  $\beta$ -hydroxyalkylamide functionality of  $\geq 3$  is a compound according to formula (II):



10. Powder coating composition, crosslinker and use  
20 according to any one of claims 1-9, characterized in  
that the second compound having a  $\beta$ -hydroxyalkylamide  
functionality of  $\leq 3$  is a compound according to  
formula (IV):



11. Use of a powder coating composition according to any  
30 one of claims 1-4 or 9-10.
12. A coated substrate, characterized in that the coating  
material is a powder coating according to any one of  
claims 1-4 or 9-10.

C L A I M S

1. Powder coating composition comprising as a binder a polymer with free carboxylic acid groups and as a crosslinker a compound containing  $\beta$ -hydroxyalkylamide groups, characterized in that the crosslinker comprises a combination of at least two compounds containing  $\beta$ -hydroxyalkylamide groups and each compound having different  $\beta$ -hydroxyalkylamide functionalities, the first compound having a  $\beta$ -hydroxyalkylamide functionality of  $\geq 3$  and the second compound having  $\beta$ -hydroxyalkylamide a functionality of  $\leq 3$ .
2. Powder coating composition according to claim 2, characterized in that the first compound has a functionality of 4 and the second compound has a functionality of 2.
3. Powder coating composition according to any one of claims 1-2, characterized in that the weight ratio between the first compound to the second compound is from 90:10 and 10:90.
4. Powder coating composition according to any one of claims 1-3, characterized in that the polymer is a polyester and/or polyacrylate.
5. Crosslinker for the preparation of a powder coating, characterized in that the crosslinker comprises a combination of at least two compounds containing  $\beta$ -hydroxyalkylamide groups and each compound having different  $\beta$ -hydroxyalkylamide functionalities, the first compound having a  $\beta$ -hydroxyalkylamide functionality of  $\geq 3$  and the second compound having a  $\beta$ -hydroxyalkylamide functionality of  $\leq 3$ .
6. Crosslinker according to claim 5, characterized in that the first compound has a functionality of 4 and the second compound has a functionality of 2.
7. Use of a combination of at least two compounds containing  $\beta$ -hydroxyalkylamide groups and each compound having different  $\beta$ -hydroxyalkylamide

The powder coatings according to Examples I, II and Comparative Example A were electrostatically applied to steel panels and cured, during 15 minutes, at 180°C.

The blister limit was determined via  
5 electromagnetic induction (see the already cited Misev, Powder Coatings, pp. 295-296).

TABLE II

10 Example blister limit in  $\mu\text{m}$

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I	120
II	140
A	105

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In I, II and A the reverse impact strength (160 inchpound), the acetone resistance (more than 100 rubs full curing), the flow (good, visually determined) and the  
20 gloss were good.

The powder coating compositions according to the present invention having the specified combinations of  $\beta$ -hydroxyalkylamides at a constant amount of benzoin yielded coatings having a desirable higher blister limit. The  
25 coatings obtained using the powder coating compositions according to the present invention also retained the desired mechanical properties.

Example II

The preparation of a powder coating based on a two- and a four-functional  $\beta$ -hydroxyalkylamide

Example I was repeated, use being made of the listed ingredients in the following amounts by weight (Table I).

TABLE I

parts by weight

Uralac P845 <sup>TM</sup>	571
Primid XL 552 <sup>TM</sup>	15
n-acetyl diethanol amine	14
15 TiO <sub>2</sub>	300
Resiflow PV-5 <sup>TM</sup>	9
Benzoin	2.5

Comparative example A

The preparation of a powder coating based on a four-functional  $\beta$ -hydroxyalkylamide

The procedure of Example 1 was repeated, to make powder coatings from the ingredients listed in the following table A in the indicated amounts by weight. No acetyl diethanol amine was added.

TABLE A

parts by weight

Uralac P845 <sup>TM</sup>	570
Primid XL 552 <sup>TM</sup>	30
TiO <sub>2</sub>	300
35 Resiflow PV-5 <sup>TM</sup>	9
Benzoin	2.5

stabilizers and catalysts can be added to the coating systems.

Suitable pigments include, for example, inorganic pigments such as titanium dioxide, zinc sulphide, iron oxide and chromium oxide, and organic pigments such as azo compounds.

Suitable fillers include, for example, metal oxides, silicates, carbonates and sulphates.

Compositions according to the invention can be used as coating agents for metal, wood and plastic substrates. Examples are general-purpose industrial top coats, top coats on machinery and equipment, in particular top coats on metal, for example for tins, domestic and other small equipment, cars and the like.

The invention will be elucidated with the following, non-restrictive examples and comparative example.

#### Example I

The preparation of a powder coating based on a combination of a two- and a four-functional  $\beta$ -hydroxy-alkylamide

In an extruder (Werner & Pfleider, ZSK 30) 570.5 parts by weight of a carboxyl-functional polyester resin (Uralac P845<sup>PM</sup>; DSM Resins B.V.) with an acid number of 35 mg KOH/g were mixed at 130°C with 20.5 parts by weight of Primid XL 552<sup>TM</sup> (compound according to formula (II); Rohm & Haas), with 9 parts by weight of n-acetyl diethanol amine (compound according to formula (IV)), with 300 parts by weight of titanium dioxide (Kronos CL 310<sup>TM</sup>), with 9 parts by weight of flow-promoting agent (Resiflow PV-5<sup>TM</sup>, Worlee), and with 2.5 parts by weight of benzoin.

After cooling, the extrudate was subjected to granulation and fine grinding to a particle size of 90  $\mu$ m.

diol, 1,2-butanediol, 1,4-butanediol, 1,3-butanediol, 2,2-dimethyl-1,3-propanediol (= neopentyl glycol), 2,5-hexanediol, 1,6-hexanediol, 2,2-[bis(4-hydroxycyclohexyl)]propane, 1,4-dimethylol cyclohexane, diethylene glycol, dipropylene glycol and 2,2-bis[4-(2-hydroxyethoxy)]phenylpropane and smaller amounts of polyols such as glycerol, hexanetriol, pentaerythritol, sorbitol, trimethylol ethane, trimethylol propane and tris(2-hydroxyethyl)isocyanurate can be used. Preferably, the alcohol component contains at least 50 mol% of neopentyl glycol and/or propylene glycol.

Additional suitable compounds for reacting with polycarboxylic acids include monoepoxides such as, for example, ethylene oxide, propylene oxide, monocarboxylic acid glycidyl ester (for example Cardura E10™; Shell) or phenyl glycidyl ether.

The polyesters are prepared, using methods known per se, by esterification or transesterification, optionally in the presence of customary catalysts such as, for example, dibutyl tin oxide or tetrabutyl titanate, a suitable choice of the preparation conditions and of the COOH/OH ratio yielding end products with an acid number between 15 and 150.

Compounds according to formula (I), (II), (III) and (IV) and methods for making them, are described in, amongst others: US-A-4727111, US-A-4788255 and EP-A-322834. The complete disclosures are incorporated herein by reference.

The preparation and testing of the powder coating can take place in a customary manner, for example as described in Misev, Powder Coatings; Chemistry and Technology (Wiley and Sons, 1991) pp. 225-226.

If desired, the powder coating can also contain mixtures of polyesters and polyacrylates. Furthermore, other resins, such as, for example, an epoxy resin, can also be included in the powder coating composition.

Of course, all the standard additives such as, for example, pigments, fillers, flow-promoting agents,



$\alpha$ - $\beta$ -methylene glutaric acid, unsaturated anhydrides, such as, for example, maleic anhydride, itaconic anhydride, acrylic anhydride and methacrylic anhydride. The polymer usually also consists of copolymerized esters of

5 (meth)acrylic acid, such as, for example, methyl methacrylate, butyl acrylate, 2-ethyl hexyl acrylate or acrylonitrile, styrene and other ethylenically unsaturated compounds.

Suitable polyesters can be obtained via standard

10 preparation methods from essentially aromatic polycarboxylic acids, such as, for example, phthalic acid, isophthalic acid, terephthalic acid, pyromellitic acid, trimellitic acid, 3,6-dichloro phthalic acid, tetrachloro phthalic acid, or, if obtainable, the anhydrides, acid

15 chlorides or lower alkyl esters thereof. Usually the carboxylic acid component is composed at least of 50% by weight, preferably at least 70 mol %, of isophthalic acid and/or terephthalic acid. Exemplary procedures are described in said reference of Misev at pages 144-162.

20 The polycarboxylic acids used can also be cycloaliphatic and/or acyclic polycarboxylic acids such as, for example, tetrahydro phthalic acid, hexahydro-endomethylene terephthalic acid, hexachloro tetrahydrophthalic acid, azelaic acid, sebacic acid, decane dicarboxylic acid,

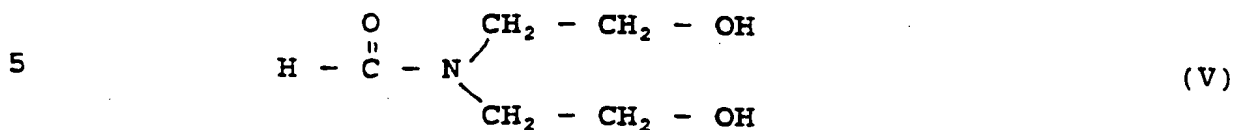
25 dimer fatty acid, adipic acid, succinic acid and maleic acid, in amounts of up to not more than 30 mol%, preferably up to not more than 20 mol%, of the total of carboxylic acids. Hydroxy-carboxylic acids and/or, optionally, lactones such as, for example, 12-hydroxy-

30 stearic acid,  $\epsilon$ -caprolactone and the hydroxypivalic acid ester of neopentyl glycol can also be used. In minor amounts, monocarboxylic acids such as, for example, benzoic acid, tert-butylbenzoic acid, hexahydro benzoic acid and saturated aliphatic monocarboxylic acids can also

35 be added during the polyester preparation.

Furthermore, especially suitable in the polyester preparation are aliphatic diols such as, for example, ethylene glycol, 1,2-propanediol, 1,3-propane-

Compounds according to formula (V) are also very suitable as compounds having a functionality of  $\leq 3$ :



The weight ratio in the crosslinker between is preferably between 90:10 and 10:90 and more preferably between 80:20 and 20:80. This ratio depends on the functionality of the polymer with free carboxylic groups.

Usually the average functionality of the polymer is between 1.7 and 4.5 and preferably between 2.3 and 3.5.

The weight ratio of the crosslinker to the polymer is usually between 10:90 and 3:97, more preferably between 20:80 and 3:97.

The acid number of the polymer containing carboxyl groups is preferably between about 15 and about 150 mg KOH/gram resin, in particular is between about 20 and about 70 mg KOH/gram resin.

The glass transition temperature,  $T_g$ , is preferably between about 30°C and about 80°C and in particular ranges between about 35°C and about 65°C.

The viscosity at 165°C ( $\eta_{\text{intra}}$ ,  $D = 17.6 \text{ s}^{-1}$ ) is preferably between about 100 and about 1000 dPas and in particular ranges between about 100 and about 800 dPas.

Said parameters influencing powder coating properties and the determination of these parameters is described at pages 175-199 and 284-300 of Powder Coatings, Chemistry and Technology by Misev (Wiley and Sons, 1991).

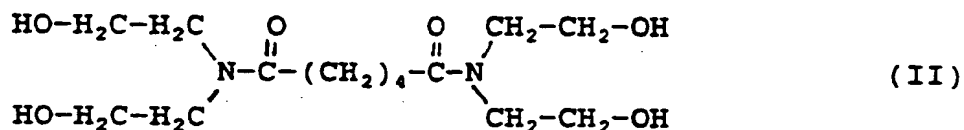
Preferably, the polymer that contains carboxyl groups is a polyester and/or a polyacrylate.

Examples of preferred monomers for polyacrylates that can be incorporated in the main chain of the polymer are unsaturated monocarboxylic acids, such as, for example, acrylic acid, methacrylic acid and crotonic acid, unsaturated dicarboxylic acids, such as, for example, maleic acid, 2-methyl maleic acid, itaconic acid, and

or hydroxy (C<sub>1</sub>-C<sub>2</sub>)-alkyl.

Preferably, the first compound having a β-hydroxyalkylamide functionality of ≥ 3 is a compound according to formula (II):

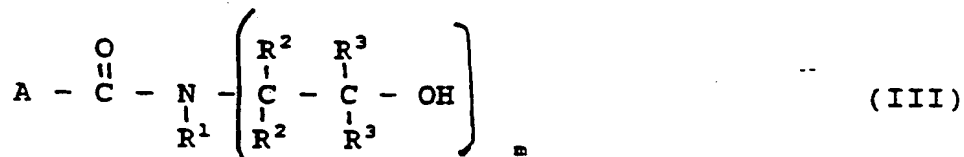
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Very suitable compounds having a β-hydroxyalkylamide functionality of ≤ 3 are compounds according to formula (I) having a β-hydroxyalkylamide functionality of ≤ 3 or compounds according to formula (III):

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wherein formula (III) A represents a monovalent group as defined for formula (I), where R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> also have the same meaning as in formula (I), and where m = 1 or 2.

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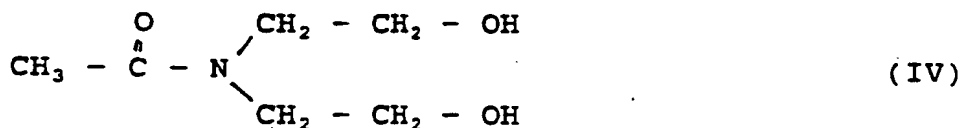
According to a further preferred embodiment of the invention in formula (I):

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A is an alkyl group with (1-10) carbon atoms, R<sup>1</sup> represents 2-hydroxyethyl or hydrogen, and R<sup>2</sup> and R<sup>3</sup> are independent of one another hydrogen or hydroxy (C<sub>1</sub>-C<sub>2</sub>)-alkyl.

Preferably, the second compound having a β-hydroxyalkylamide functionality of ≤ 3 is a compound according to formula (IV):

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Preferably, the functionality of the second compound having a functionality of ≤ 3 according to formula (I) is 2.

- A represents a mono- or polyvalent organic group derived from a saturated or unsaturated alkyl group with 1-60 carbon atoms (for example ethyl, methyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, eicosyl, triacontyl, tetracontyl, pentacontyl and hexacontyl); an aryl group, such as for example phenyl, naphthyl; a trialkylene amino group with 1-4 carbon atoms per alkylene group, for example trimethylene amino and triethylene amino; or an unsaturated residue with one or more alkenic groups ( $-C=C-$ ) with 1-4 carbon atoms, such as, for example, ethenyl, 1-methyl ethenyl, 3-butenyl-1,3-diyl and 2-propenyl-1,2-diyl, carboxy-alkenyl group, for example 3-carboxy-2-propenyl group, an alkoxy carbonyl-alkenyl group with 1-4 carbon atoms, such as, for example, 3-methoxy carbonyl-2-propenyl group;

-  $R^1$  represents hydrogen, an alkyl group with 1-5 carbon atoms (for example methyl, ethyl, n-propyl, n-butyl, sec. butyl, tert. butyl and pentyl) or a hydroxy-alkyl group with 1-5 carbon atoms (for example 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 4-hydroxybutyl, 3-hydroxybutyl, 2-hydroxy-2-methylpropyl, or the hydroxy derivatives of the pentyl isomers);

-  $R^2$  and  $R^3$  are the same or different and each independently represents hydrogen or a straight or branched alkyl group with 1-5 carbon atoms, while one of the groups  $R^2$  and one of the groups  $R^3$  may also form, together with the adjacent carbon atoms, a cycloalkyl group, such as, for example, cyclopentyl and cyclohexyl;  $R^2$  and  $R^3$  may also be hydroxyalkyl groups, such as, for example, hydroxy ( $C_1-C_5$ )-alkyl groups, hydroxymethyl and 1-hydroxyethyl, being preferred among the latter and

- the  $\beta$ -hydroxyalkylamide functionality is  $\geq 3$ . Preferably, the functionality is 4.

According to a further preferred embodiment of the invention in formula (I):

A is an alkyl group with (1-10) carbon atoms,  $R^1$  represents 2-hydroxyethyl or hydrogen, and  $R^2$  and  $R^3$  are independent of one another hydrogen

the cured powder coating at a temperature of 200°C for a prolonged period of time (for example between 30 and 60 minutes). This discolouration upon excessive curing (yellowing on overbake) increases with the amount of benzoin. A lower amount of benzoin, on the other hand, results in a lower blister limit, such as lower than 60  $\mu\text{m}$ , which results in surface defects.

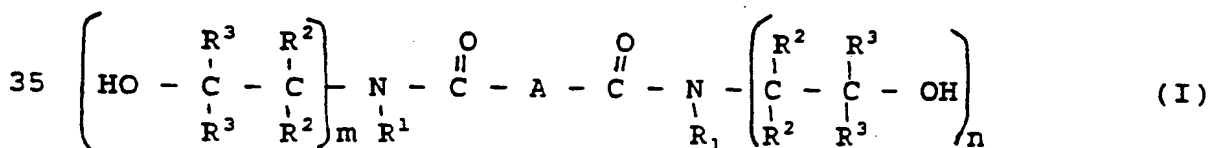
The object of the invention is to provide a powder coating composition in which it is possible to use a small amount of benzoin, for example between 0.05 and 0.8 wt.%, to obtain the highest possible blister limit, for example higher than 120  $\mu\text{m}$ . Of course, the powder coatings must also retain good mechanical properties, such as, for example, good gloss, toughness and impact resistance and chemical properties such as for example a good chemical resistance.

The invention is characterized in that the crosslinker comprises a combination of at least two compounds containing  $\beta$ -hydroxyalkylamide groups and each compound having different  $\beta$ -hydroxylalkylamide functionalities, the first compound having a  $\beta$ -hydroxyalkylamide functionality of  $\geq 3$  and the second compound having a  $\beta$ -hydroxyalkylamide functionality of  $\leq 3$ .

The functionality stands for the average number of  $\beta$ -hydroxyalkylamide groups per molecule.

As a result, powder coatings are obtained in which the blister limit has been raised considerably while the desired mechanical and chemical properties are retained.

Suitable compounds containing  $\beta$ -hydroxyalkylamide groups and having a functionality of  $\geq 3$  can be depicted structurally according to formula (I):



where:

## POWDER COATING COMPOSITION WITH HYDROXYALKYLAMIDE CROSSLINKER

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The invention relates to a powder coating composition comprising as a binder a polymer with free carboxylic acid groups and as a crosslinker a compound containing  $\beta$ -hydroxyalkylamide groups.

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A powder coating comprising a co-reactable mixture of an amorphous carboxylic acid group containing polyester and a  $\beta$ -hydroxyalkylamide is known from EP-A-322834. The composition described in this application is cured - after application to a substrate - by heating the powder to 160-200°C so that the powder melts, forming a smooth layer. At that temperature the coating is chemically crosslinked due to an esterification reaction between the acid groups of the polymer and the hydroxy groups of the compound containing  $\beta$ -hydroxyalkylamide groups. According to EP-A-322834, a de-gasifying agent, benzoin (0.5 to 3% by wt. of the powder composition), may be added to the composition. A de-gasifying agent is needed to ensure that the air and/or water entrapped due to melting of the powder (during a curing cycle) are removed from the paint layer as a result of the reaction. Any gas bubbles that remain in the coating reduce the adhesion of the coating to the substrate and markedly adversely affect the protection obtainable with the coating.

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Although coatings of this composition are characterized in EP-A-322834 as having good physical properties, such compositions are unsuitable for preparing a white or crystal-clear coating because the powder coating exhibits some degree of browning after curing, as indicated in Mercurio, New Perspective on Hydroxyamide Crosslinkers, 16th International Conf. in Org. Sci. and Tech. 235-49 (Athens, Greece 1990).

35

Also, browning appears to intensify upon heating

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<b>(21) International Application Number:</b> PCT/NL93/00155 <b>(22) International Filing Date:</b> 21 July 1993 (21.07.93)  <b>(30) Priority data:</b> 9200687 29 July 1992 (29.07.92) BE  <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> STANSSENS, Dirk, Armand, Wim [BE/NL]; Pastoorstindestraat 75 B1, B-3620 Lanaken (BE). VAN DEN ELSHOUT, Wilhelmus, Henricus, Hubertus, Antonius [NL/NL]; Onderstehof 9, NL-6132 SM Sittard (NL). HOUWELING, Marten [NL/NL]; Engelsmanplaat 113, NL-8032 DX Zwolle (NL).		<b>(74) Agent:</b> SCHMEETZ, Marcel, Max, Hubertina, Johanna; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).  <b>(81) Designated States:</b> AU, FI, JP, NO, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> POWDER COATING COMPOSITION WITH HYDROXYALKYLAMIDE CROSSLINKER  <b>(57) Abstract</b>  The invention relates to a powder coating composition comprising as a binder a polymer with free carboxylic acid groups and as a crosslinker a compound containing $\beta$ -hydroxyalkylamide groups. The crosslinker comprises a combination of at least two compounds containing $\beta$ -hydroxyalkylamide groups and each compound having different $\beta$ -hydroxyalkylamide functionalities, the first compound having a $\beta$ -hydroxyalkylamide functionality of $\geq 3$ and the second compound having a $\beta$ -hydroxyalkylamide functionality of $\leq 3$ .		